



Processes controlling the concentration of hydroperoxides at Jungfraujoch Observatory, Switzerland

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**Hydroperoxides at
Jungfraujoch
Observatory**

S. J. Walker et al.

Processes controlling the concentration of hydroperoxides at Jungfraujoch Observatory, Switzerland

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀◀

▶▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Abstract

An automated, ground-based instrument was used to measure gas-phase hydroperoxides at the Jungfraujoch High Altitude Research Station as part of the Free Tropospheric EXperiment (FREETEX) during February/March 2003. A nebulising reflux
5 concentrator sampled ambient air twice hourly, prior to on-site analysis by HPLC specification, coupled with post-column peroxidase derivatisation and fluorescence detection. Hydrogen peroxide (H_2O_2) concentrations reached up to 1420 pptv over the 13-day period with a mean of 206 ± 261 pptv (\pm one standard deviation). Methyl hydroperoxide (CH_3OOH) reached up to 921 pptv with a mean of 76 ± 96 pptv. No other organic
10 hydroperoxides were detected. The lack of an explicit diurnal cycle suggests that hydroperoxide concentrations are chiefly influenced by transport processes rather than local photochemistry at this mountainous site. We find elevated concentrations of H_2O_2 in air masses originating from the south-west indicative of higher concentrations of HO_x due to more active photochemistry. Air which has been recently polluted exhibits low
15 H_2O_2 concentration due to a combination of suppression of HO_2 by NO_x and deposition. We also conclude that despite being at a high alpine site, the vast majority of the air observed was extensively influence by the boundary layer during our campaign (diagnosed from high CO concentrations and the high NO_x to NO_y ratio) resulting in deposition of H_2O_2 to the surface and hence reduced H_2O_2 concentrations. The concentrations of H_2O_2 sampled here are consistent with previous box modelling studies
20 of hydroperoxides which invoked a depositional sink.

1 Introduction

Hydroperoxides play an important role in gas-phase free radical chemistry of the atmosphere and in the aqueous-phase chemistry of acid precipitation. Hydroperoxides
25 such as hydrogen peroxide (H_2O_2) and methyl hydroperoxide (CH_3OOH) are produced through the self-reaction of peroxy radicals (hydroperoxy, HO_2 and organic peroxy,

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6, 7177–7205, 2006

Hydroperoxides at Jungfraujoch Observatory

S. J. Walker et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

EGU

RO₂) (e.g. Lee et al., 2000). These peroxy radicals are intimately linked to ozone production and loss, leading to hydroperoxides being a key diagnostic of the chemical state of the atmosphere. The chemistry of the O_x, HO_x and RO_x is summarized in Fig. 1. H₂O₂ is also a major oxidant of SO₂ in clouds (Penkett et al., 1979) so alongside O₃ and OH, its measurement is needed to assess the oxidative capacity of the atmosphere.

Previous analyses of H₂O₂ and CH₃OOH observations have identified key physical and chemical processes controlling their concentration (e.g. Heikes et al., 1987). As shown in Fig. 1, the production of H₂O₂ is controlled by the abundance of HO₂, which shows sensitivity to HO_x (OH and HO₂) production, loss and recycling. Formation of peroxy radicals is predominantly through the photo-oxidation of carbon monoxide (CO) and volatile organic compounds (VOC), by the OH radical (detailed in Lightfoot et al., 1992). A second significant source is from formaldehyde (CH₂O), which undergoes photolysis and reaction with OH to produce HO₂.

Air-masses rich in NO_x tend to show lower H₂O₂ concentrations as peroxy radicals oxidise NO to NO₂ rather than self-reacting to form H₂O₂ (Tremmel et al., 1993; Penkett et al., 1995) and total radical loadings are suppressed by HNO₃ production through the reaction of OH with NO₂ radicals (Poppe et al., 1993). According to Lee et al. (2000), substantial suppression of hydroperoxide production occurs at NO concentrations exceeding 100 pptv. In contrast, it is calculated that NO concentrations below 3 to 20 pptv are needed for hydroperoxide production to dominate (Reeves and Penkett, 2003; Crutzen and Zimmermann, 1991; Finlayson-Pitts and Pitts, 1986). Such low concentrations of NO can only be found in very remote regions of the troposphere lacking NO_x sources.

Lower concentrations of H₂O₂ are observed in air masses exposed to the ground or clouds due to dry and wet deposition (e.g. Kleinman, 1986; Heikes et al., 1987; Chandler et al., 1988; Gallagher et al., 1991). Rapid loss of gaseous H₂O₂ into clouds is due to a high Henry's law coefficient of H₂O₂ (H_{H₂O₂} is 7.73×10⁴ M atm⁻¹ at 298 K, Sander et al., 2003) and rapid oxidation of S(IV) species to S(VI) within the aqueous

Hydroperoxides at Jungfraujoch Observatory

S. J. Walker et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

phase. Other important H_2O_2 and CH_3OOH sinks are their reaction with OH radicals and photolysis at ultraviolet wavelengths generating OH and in the case of CH_3OOH , OH and CH_3O .

The aim of this paper is to investigate the impact of these chemical and physical processes on the concentration of H_2O_2 and CH_3OOH at a remote mountainous site and to understand the usefulness of H_2O_2 observations as a diagnostic of the atmospheric compositional system.

2 Experimental

2.1 Site description

The observations are from the FREE Tropospheric EXperiment (FREETEX) that took place in February to March 2003 at the Sphinx Observatory, Jungfraujoch High Altitude Research Station (7.98°E , 46.55°N) (subsequently referred to as JFJ) situated at 3580 m above mean sea level (a.m.s.l.). There have been three previous FREE-TEX campaigns in 1996, 1998 and 2001 at this site (Zanis et al., 1999, 2000a, b, 2003; Carpenter et al., 2000). The Sphinx Observatory resides in a saddle between the two alpine summits, Jungfrau (4155 m a.m.s.l.) to the south-west and Mönch (4099 m a.m.s.l.) to the north-east, in the Swiss Alps. This leads to mainly north-westerly and southerly air masses reaching the station. The site characteristics are described in Zellweger et al. (2003). The observatory is usually thought to be located in the lower free troposphere (FT) in winter and early spring but can experience planetary boundary layer (PBL) air (Carpenter et al., 2000), especially in the summer when convection is enhanced (Baltensperger et al., 1997; Lugauer et al., 1998, Zellweger et al., 2003). The high altitude site is thought to experience few local emission sources, and therefore can offer ideal conditions for long-term sampling of free tropospheric air. The JFJ is incorporated in the Swiss National Air Pollution Monitoring Network (NABEL), which is maintained by EMPA Dübendorf on behalf of the Swiss Federal Office for the

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Environment (FOEN). Among other species, NO, NO₂, O₃ and CO are measured routinely and are available with a time resolution of 30 min. All meteorological parameters are measured by the Federal Office of Meteorology and Climatology (MeteoSwiss). Due to the importance of monitoring long-term trends of gaseous and aerosol parameters in the free troposphere, the JFJ station has been incorporated into the Global Atmosphere Watch (GAW) program of the World Meteorological Organization (WMO) as a Global GAW Station.

2.2 Method for hydroperoxide sample collection and analysis

Sample collection took place at the Sphinx laboratory between the 27 February and the 12 March 2003. Figure 2 shows a schematic diagram of the analytical system. Samples were obtained from the gas-phase using an amber-glass nebulising reflux concentrator (Fig. 2) based on the design by Cofer et al. (1985). Atmospheric air was drawn by a vacuum pump from the NABEL inlet (previously described in Zellweger et al., 2000), through ~5 m 1/4" OD Teflon (perfluoroalkoxy) tubing into the nebuliser, at a flow rate of 2.7 l min⁻¹. The residence time in the inlet tubing was less than 4 sec. A sampling time of 25 min provided sufficient concentration of the solution for analysis. Collection efficiencies of 75±3% and 40±2% have been previously determined experimentally for H₂O₂ and CH₃OOH respectively and were assumed in this study (Jackson and Hewitt, 1996; Morgan, 2004).

Once collected, aqueous samples were injected through a 0.2 µm filter onto the HPLC where hydroperoxide speciation was achieved using a C-18 reversed-phase column. Helium-degassed mobile phase was supplied at a flow rate of 0.6 ml min⁻¹. Post-column, the hydroperoxide components were derivatised in a reaction coil in the presence of horseradish peroxidase to form a stable dimer, based on the technique developed by Lazrus et al. (1985, 1986). The derivatisation reagent was raised to pH 5.8 by the addition of potassium hydroxide (1 M) and buffered by potassium hydrogen phthalate (0.5 M). A peristaltic pump delivered the derivatisation reagent at constant rate of 0.25 ml min⁻¹. The pH was then raised above 10 to produce the fluorescent anionic

Hydroperoxides at Jungfraujoch Observatory

S. J. Walker et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

dimer form via a Nafion membrane submerged in 100 ml NH_4OH (30%). Detection was achieved using a fluorescence spectrophotometer with excitation and emission wavelengths of 305 and 410 nm respectively, via a xenon short arc lamp. Calibration of the system was carried out daily. Further details of this method can be found in Morgan and Jackson (2002). Based on three and ten times the standard deviation of the base line noise, the instrument limit of detection and quantification at 95% confidence (Taylor, 1987) during the campaign was found to be 21 and 68 pptv respectively.

2.3 Other measurements

An overview of measurement techniques including detection limits and uncertainties of O_3 , CO , NO_x and NO_y can be found in Zellweger et al. (2000) and for toluene and benzene in Reimann et al. (2004). A further suite of species, namely NMHCs, CO , O_3 , PAN and the photolysis rate coefficient, $j(\text{O}^1D)$, were measured throughout the campaign by the University of Leeds (School of Chemistry) and are described in Whalley et al. (2004).

3 Results and discussion

3.1 General observations

Figure 4 presents the 13-day time series for H_2O_2 and CH_3OOH for the sampling period. H_2O_2 ranged from below the limit of detection (21 pptv) up to 1420 pptv with an average concentration of 206 ± 261 pptv (\pm one standard deviation). Table 1 presents this data alongside previous measurements at other high altitude sites and from aircraft. The observations made during this campaign are consistent with previous measurements. More specifically they are within the range of previous H_2O_2 measurements at this site and other Alpine sites (<100 – 6000 pptv) (Dommen et al., 1995; Sigg et al., 1992; Lehman et al., 1992). However, the observed mean for H_2O_2 appears lower than

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

those previously observed at alpine sites. This may be because the previous measurements were made during the summer, included forested areas (where hydroperoxides can be produced through biogenic hydrocarbon oxidation), and also excluded periods of cloud or rain (so concentrations were not reduced through wet deposition). Although direct comparison between these datasets is difficult we conclude that our observational dataset appear consistent with previous observations.

CH₃OOH was observed during this campaign and ranged from below the detection limit, up to 921 pptv, with a mean mixing ratio of 76±96 pptv. There are no previously published CH₃OOH measurements for this site. Again these observations are consistent with previous observations at other sites (see Table 1). No other higher hydroperoxides were detected. This will be discussed in more detail in Sect. 3.7.

3.2 Effect of local and synoptic scale meteorology

Mean diurnal cycles for H₂O₂ and CH₃OOH are shown in Fig. 5. There is some suggestion of a maximum in peroxide concentrations during the day indicative of photochemical production (e.g. Dommen et al., 1995). However, there is significant variability, suggesting a large role for meteorology in determining the levels of hydroperoxides sampled.

Four hydroperoxide maxima were observed on the 1, 6, 9 and 11 March. The vector-averaged local wind direction throughout the campaign was north-westerly (312°) with no significant change in the mean local wind direction during these maxima. Thus, the local wind direction appears to offer little information on the magnitude of the hydroperoxide concentration.

Back trajectories were calculated each 6 h of the campaign using ECMWF analysed winds at 2.5×2.5° resolution and 31 levels using 3-D vertical advection via the BADC Trajectory Service (<http://badc.nerc.ac.uk>). These trajectories agreed well with plots calculated using the FLEXTRA Trajectory Service (<http://zardoz.nilu.no/~andreas/flextra+flexpart.html>), which offers a finer resolution (1.125×1.125°) appropriate for the Alpine region. The “synoptic wind direction” (diagnosed from the last day of transport

Hydroperoxides at Jungfraujoch Observatory

S. J. Walker et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

described by the trajectory) was in general from the west/north-west (consistent with the observed wind direction) except during the 28 February to 2 March, 5 to 6 and 10 to 12 March when air-masses with a south-westerly character were sampled (see Fig. 3 for examples of these trajectories). Three of the four hydroperoxide maxima occurred on the arrival of these synoptic south-westerly air-masses (1, 6 and 11 March). The maxima observed on the 9 March was during a period of north-westerly air (see Fig. 3), and is discussed separately in Sect. 3.4.

During south-westerly flow, primary photochemical pollutants e.g. CO and NO_x, were often enhanced, as illustrated in Whalley et al. (2004) for this campaign and previously seen in past campaigns at this site (Forrer et al., 2000; Carpenter et al., 2000). As described earlier, the relationship between hydroperoxides and primary pollutants (notably NO_x) is complicated. Hydroperoxide concentrations were sensitive to the NO_x concentration within these air-masses. High hydroperoxide concentrations were only present when NO_x concentrations were low. These air-masses were often photochemically aged, as demonstrated by a lower NO_x/NO_y ratio. Chin et al. (1994) used the distinction of a NO_x/NO_y ratio of <0.3 to evaluate when an air-mass could be described as photochemically aged. Air-masses with ratios significantly above this can therefore be classed as recently polluted. Secondly, the toluene/ benzene ratio was also used to support this classification, where values below 0.5 were indicative of aged air-masses due to the shorter atmospheric lifetime of toluene compared to benzene (Li et al., 2006).

Using these classifications, the high NO_x levels during 6 March, which in combination with wet and dry deposition in the humid ascending air-mass caused hydroperoxide concentrations to reduce, can therefore be classed as fresh emissions (NO_x/ NO_y~0.8) within a south-westerly, ascended air-mass (from 750–850 hPa, ~2 km). The toluene to benzene ratio increased from a background level (the campaign median of ~0.5) to values above 1.5, which was also indicative of fresh emissions at this site (Li et al., 2006a). The sources of these south-westerly air-masses appeared to be the industrialised region of the Valais Valley (southern Switzerland) or the Po Valley (northern

Hydroperoxides at Jungfraujoch Observatory

S. J. Walker et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Italy), consistent with Seibert et al. (1998) and Forrer et al. (2000). The latter found that the highest CO (double the average value) and NO_x (>1 to <10 ppbv) concentrations were associated with winds that transported anthropogenic pollution to this site from these industrialized regions of Switzerland and Italy. Similar conditions to those described by Forrer et al. (2000) occurred on 6 March when a doubling of CO (>190 ppbv) and intense NO_x (~4 ppbv) was observed. Their paper described upslope motion associated with this south-westerly flow, as a process of transporting polluted air from lower altitudes to the site. The importance of these processes at this site was highlighted by Carpenter et al. (2000), who observed diurnal CO and H₂O cycles indicative of daily upslope motion, and was developed further by Zellweger et al. (2003).

Thus much of the variability seen in the hydroperoxide concentrations observed can be attributed to changes in flow regime leading to changes in the levels of photo-pollutants rather than local changes in photolysis rates.

3.3 Sampling of boundary layer and free tropospheric air

Mountain sites such as JFJ are often thought to offer sampling within the free troposphere. In the previous section we have shown that there are examples of boundary layer air being sampled. Quantifying the fraction of boundary layer air sampled is important for placing the observations made at this site into a context, and is described e.g. in Zellweger et al. (2003).

The mean CO observed during the campaign was 140±14 ppbv consistent with the seasonal cycle of CO previously measured at JFJ (Rinsland et al., 2000; Forrer et al., 2000; BUWAL, 2005). Carpenter et al. (2000) used the criteria of CO <200 ppbv, NO_x/NO_y<0.3, and a coarse screening of cloudy days, by excluding periods when global radiation was below the campaign median, to diagnose being within the free troposphere. Data collected as part of this campaign fulfilled these criteria for only 4% data coverage, which was lower than previous research of Carpenter et al. (2000) at this site, where free tropospheric air amounted to 17% using the same criteria during FREETEX 1998. Various other criteria have been used to define free tropospheric air

Hydroperoxides at Jungfraujoch Observatory

S. J. Walker et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

for longer campaigns at this site, with free tropospheric periods making up 40% during March to August 1997 and 1998 (Zellweger et al., 2003) and 57% during 1993 to 1997 (Li et al., 2006¹) of the measurement period. The low proportion of free tropospheric air during our campaign indicated that mainly boundary layer air was sampled and highlights the need for long-term sampling at mountainous sites to allow a larger proportion of undisturbed free tropospheric air to be sampled. The periods that satisfied free tropospheric criteria occurred for a short time on the 6 March and for longer periods towards the end of the campaign (9 to 12 March). Both examples corresponded to elevated hydroperoxide levels, most likely due to a removal of dry deposition as a hydroperoxide sink.

Previous aircraft measurements of free tropospheric H₂O₂ have found a significant correlation between H₂O₂ and the product of its precursors, O₃ and H₂O (Penkett et al., 1995, 1998; Weinstein-Lloyd et al., 1998). The lack of a significant correlation ($R^2 < 0.1$) found from this dataset again implies that the simple free tropospheric assumptions made in these papers are not appropriate at this site (i.e. all three papers used altitudes >1500 m and Weinstein-Lloyd et al. (1998) also used a coarse particle count of <10 cm⁻³ to remove periods of cloud). After applying Carpenter et al. (2000) criteria to determine only those periods where air was sampled within the free troposphere, a weak positive correlation was then observed ($R^2=0.3$).

Most of the air observed during the campaign had a significant influence of the boundary layer. Occasions of free tropospheric air were observed, associated with higher hydroperoxide concentrations; however they contributed negligibly to the overall dataset. This reinforces the importance of the established filtering methods for free tropospheric air, to stringently select data from mountainous sites, especially when short-term campaigns as described in this research are undertaken.

¹Li, Y., Staehelin, J., Auvray, M., Bey, I., and Schultz, M.: Comparison between numerical simulations of two 3-D global models (GEOS-CHEM and MOZART) with ozone observations at Jungfraujoch (Switzerland) and ozone sondes from Payerne, Atmos. Environ., submitted, 2006.

Hydroperoxides at Jungfraujoch Observatory

S. J. Walker et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

3.4 Impact of high and low NO_x on hydroperoxides

It was shown earlier that higher concentrations of photo-pollutants in south-westerly air can lead to enhanced hydroperoxide concentrations. The three examples of south-westerly flow experienced during the campaign are described in Table 2, together with a fourth example of enhanced hydroperoxides in a north-westerly air-mass.

In the early morning of 6 March (Example A, Table 2), high levels of hydroperoxides (1.0 and 0.4 ppbv H₂O₂ and CH₃OOH respectively) occurred in drier, south-westerly air that had remained at relatively constant altitude (600–700 hPa), with relatively low CO (~110 ppbv) and NO_x levels (~0.3 ppbv), compared to the rest of the campaign. However, a spike in NO_x of over 1 ppbv, at 07:00 caused a brief, partial reduction in hydroperoxides, due to suppression of HO₂ by elevated NO_x. This air-mass displayed a moderate NO_x to NO_y ratio (~0.6), together with a relatively large increase in longer-lived alkanes compared to small increases in short-lived alkenes (see Whalley et al., 2004). These observations suggest slight photochemical aging and could be caused by some vertical mixing into the air-mass, by aged air from ~650 hPa (~5 km), 5 days earlier (see black line, bottom left panel, in Fig. 3). Hydroperoxides were therefore sustained in this event by a combination of photochemically aged air with an abundance of HO_x, low NO_x, and little surface deposition.

In the afternoon of the 6 March (Example B, Table 2), freshly emitted NO_x in a moist air-mass (relative humidity >80%) arrived from the south-west and caused the suppression of hydroperoxides for over 10 h. This increase in NO_x was due to a shift to ascended air (from 750–850 hPa, see light blue and green lines, Fig. 3) that also exhibited enhanced CO (>150 ppbv). NO concentrations detected during this period were five times the level that Lee et al. (2000) (>100 pptv) showed, which resulted in substantial suppression of hydroperoxide production alongside increased hydroperoxide deposition. Hydroperoxides were therefore reduced by a combination of high NO (average of 64 pptv) that competed with peroxy radical self-reactions, high NO₂ (average of 2450 pptv) for several hours, providing a sink for OH (e.g. Poppe et al., 1993), wet de-

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

position (see Sect. 3.5) and contact with the surface, allowing increased dry deposition of H_2O_2 .

During 11 to 12 March (Example C, Table 2), back-trajectories showed a south-westerly air-mass that had descended from 400–600 hPa over 5 days, with little influence of air from lower altitudes (see blue lines in bottom right panel, Fig. 3). This very dry air ($\text{RH} < 20\%$) had a low NO_x/NO_y ratio (< 0.3) and so can be considered as photochemically aged (Chin et al., 1994). To support this classification, 11 to 12 March also showed toluene/benzene ratios below 0.5 (Li et al., 2005). Although CO remained around 140 ppbv, the relatively long lifetime of CO (~ 60 days) (Volz et al., 1981) compared to other photochemical tracers, means this air-mass could still have been of free tropospheric origin. This air-mass could therefore become rich in hydroperoxides because, little dry deposition could occur and there was a lack of NO_x which prevented the competing reactions to H_2O_2 and CH_3OOH production. The high concentrations of hydroperoxides imply that HO_x was readily available.

During 9 to 10 March (Example D, Table 2), a descending north-westerly also gave observed hydroperoxide maxima alongside a NO_x to NO_y ratio of ~ 0.4 . This aged air-mass had descended from ~ 500 hPa for the previous 5 days (see green and orange lines, top panel, Fig. 3). Again a lack of NO_x and dry deposition allowed hydroperoxides to accumulate, but these peaks are less intense than for the previous examples (A to C) that arrived in south-westerly air, which supports the findings that more HO_x was available in south-westerly air-masses, which have been subjected to more intense sunlight and so have enhanced radical concentrations.

Overall we find that oxides of nitrogen have a significant impact on the concentrations of hydroperoxides. Air coming from the south-west with moderate levels of NO_x exhibits significantly higher hydroperoxide concentration than air which is more significantly polluted air, or air coming from the north. This is due to a combination of a history of higher photolysis rates and water vapour concentration, leading to enhanced HO_x production in south-westerly air, with also reduced HO_x loss and lower OH to HO_2 ratios due to the moderate NO_x concentrations.

Hydroperoxides at Jungfraujoch Observatory

S. J. Walker et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

3.5 Wet deposition and cloud processing

Unlike the case on the 6 March, the decrease in hydroperoxide concentration observed on the 1 March was not due to a combination of deposition and an increase in NO_x . The trajectories showed a change to an ascending air-mass, associated with an increase in relative humidity ($>90\%$) and increased deposition, but no increases in NO_x were observed. Dilution effects with an air-mass that had been exposed to increased dry deposition to the surface could therefore have been partly responsible for the observed reduction in hydroperoxides. The high humidity indicates that cloud processing had also occurred. Previous studies have shown that air-masses exposed to cloud processing exhibit lower concentrations of H_2O_2 due to wet deposition (e.g. Heikes et al., 1987; Chandler et al., 1988; Gallagher et al., 1991). As to be expected, H_2O_2 observed during this event reduced faster than CH_3OOH (by a factor of ~ 2.4) due to its much higher solubility. However, the ratio of the Henry's Law coefficients ($H_{\text{H}_2\text{O}_2}/H_{\text{CH}_3\text{OOH}} \sim 260$) implies that CH_3OOH should be taken up by water droplets by a factor of ~ 100 times less than this, relative to H_2O_2 . This rapid uptake of CH_3OOH relative to H_2O_2 could imply that processes exist at the JFJ to facilitate its uptake into water droplets. However the exact mechanism leading to this enhanced loss of CH_3OOH relative to H_2O_2 and the magnitude of the role of dilution is unclear.

3.6 Agreement with a previous photochemical box model

Zanis et al. (1999) described constrained box modelling work of the radicals at the JFJ site during April to May 1996. However, at the time of their study, observations of hydroperoxides were not available to help constrain their modelling effort. Their work simulated H_2O_2 concentrations in the order of a magnitude, from 1700 to 170 pptv without and including dry deposition respectively. The mean observed H_2O_2 observations of 206 ± 261 pptv during this campaign are thus much more consistent with the calculations that include a surface depositional sink. Meteorological conditions during the 1996 campaign were comparable to our campaign in 2003, with similar temperature,

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

pressure and wind speeds, and consistent concentrations of O_3 and water vapour. The main differences between the two campaigns were the lower CO , $j(O^1D)$ and NO measured in 2003 compared to 1996. The variations in the concentrations of photochemical pre-cursors to H_2O_2 between the two campaigns alone, is not sufficient to account for an order of a magnitude difference between the previously modelled concentration of H_2O_2 without a depositional sink and our observations. Again we conclude that depositional processes are critical at this site for determining hydroperoxide concentration.

Mean NO levels during this 2003 campaign were low (~ 19 pptv), which places the site during the observation period slightly below the NO regime (20 to 100 pptv) set by Zanis et al. (1999) for simultaneous O_3 and H_2O_2 production. H_2O_2 can be produced alongside O_3 in this regime because there is sufficient NO to lead to O_3 production, but peroxy radical combination reactions are still able to dominate over the loss of OH through NO_2 . During the campaign, the data selected using the criteria of Carpenter et al. (2000) for free tropospheric air, also did not display a significant anti-correlation between O_3 and H_2O_2 ($R^2=0.2$). This is consistent with simultaneous production of both O_3 and H_2O_2 but is in contrast to the previously observed anti-correlation between O_3 and H_2O_2 for the free troposphere (e.g. Ayers et al., 1992). Again this observational evidence strongly supports the case that the JFJ station mainly observed boundary layer air during this campaign and did not strongly sample the free troposphere (even during periods where “free tropospheric” criteria were satisfied).

The box modelling described by Zanis et al. (1999) is only consistent with the hydroperoxide observations made during this study if there is a significant and sustained surface depositional sink of the hydroperoxides. Thus even at this high altitude mountain site, the impact of the boundary layer cannot be ignored and as a consequence, filtering and data flagging of air disturbed by the surface is essential.

3.7 Other hydroperoxides

The oxidation of hydrocarbons within the atmosphere should lead to the production of a large number of hydroperoxides. Previous observations have detected hydroxymethyl

Hydroperoxides at Jungfraujoch Observatory

S. J. Walker et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

hydroperoxide (HOCH_2OOH) peroxyacetic acid ($\text{CH}_3\text{C}(\text{O})\text{OOH}$), and ethylhydroperoxide ($\text{C}_2\text{H}_5\text{OOH}$) at this altitude (Fels and Junkermann, 1994; Weinstein-Lloyd et al., 1998; Crounse et al., 2005, private communication). However, they were not observed during this study. This is surprising given that two of these species have higher solubility than H_2O_2 and CH_3OOH respectively ($H_{\text{HOCH}_2\text{OOH}} = 1.7 \times 10^6 \text{ M atm}^{-1}$, Sander et al., 2003, and $H_{\text{CH}_3\text{C}(\text{O})\text{OOH}} = 473 \text{ M atm}^{-1}$, Seinfeld and Pandis, 1998), which should permit more efficient collection via this technique (giving ~ 94 and $\sim 43\%$ respectively based on the sampler collection efficiency and the Henry's Law Constant for these compounds). Using these collection efficiencies and the limit of detection for the instrumental set-up, an upper limit of ~ 22 and ~ 48 pptv can therefore be stated for HOCH_2OOH and $\text{CH}_3\text{C}(\text{O})\text{OOH}$ respectively. The collection efficiency is expected to be low ($< 40\%$) for hydroperoxides less soluble than CH_3OOH , such as $\text{C}_2\text{H}_5\text{OOH}$, meaning that concentrations must be above 50 pptv to be sampled successfully.

Fels and Junkermann (1994) observed levels of HOCH_2OOH up to 550 pptv at a mountainous alpine site (1780 m a.m.s.l.), and reported that CH_3OOH and HOCH_2OOH were the dominant ROOH, with $\text{C}_2\text{H}_5\text{OOH}$ and $\text{CH}_3\text{C}(\text{O})\text{OOH}$ contributing $< 10\%$. However, their research was conducted during summer, and at lower altitude, where sources of ROOH are more abundant. In comparison, the JFJ measurements were made during early spring when concentrations would be expected to be lower. A more recent study by Valverde-Canossa et al. (2005) inferred ROOH concentrations from aqueous-phase cloud water samples at a mountainous site in Germany (937 m a.m.s.l.) with CH_3OOH , HOCH_2OOH and 1-hydroxyethyl hydroperoxide ($\text{CH}_3\text{CH}(\text{OH})\text{OOH}$) concentrations of < 40 , < 0.020 and < 3.5 pptv respectively. These levels of ROOH were below the detection limit of the analytical instrument used at JFJ.

Significant levels of $\text{CH}_3\text{C}(\text{O})\text{OOH}$ (100–300 pptv) were observed in the recent INTEX-NA aircraft campaign at the same altitude as JFJ over the Atlantic coast of USA (Crounse et al., 2005, private communication]. Observations of H_2O_2 during the INTEX-NA campaign were a factor of as much as 10 higher than were observed during this JFJ campaign. Thus if the $\text{CH}_3\text{C}(\text{O})\text{OOH}$ concentrations scales with H_2O_2 con-

Hydroperoxides at Jungfraujoch Observatory

S. J. Walker et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

centrations, we would expect concentrations of $\text{CH}_3\text{C}(\text{O})\text{OOH}$ of around 10–30 pptv, which is below the detection limit and thus would not be detected with this instrument. It seems likely that other hydroperoxides are present in the atmosphere at JFJ. However, their expected concentrations are likely to be below those that can be observed by the current instrumental set-up.

4 Conclusions

Gas-phase hydroperoxide measurements were made at Jungfraujoch High Altitude Research Station as part of the FREETEX campaign during February and March 2003. These are the first speciated hydroperoxide measurements for this site, providing a quantitative assessment of both inorganic and organic hydroperoxide concentrations. H_2O_2 and CH_3OOH were detected but no other hydroperoxides were detected, consistent with our understanding of their concentrations within the atmosphere. Although a diurnal cycle in both H_2O_2 and CH_3OOH was observed, it was not strong because of meteorologically-driven variability. Air masses from the south-west typically showed higher hydroperoxide concentrations due to enhanced photochemistry. Air masses which had been exposed to high levels of recent pollution showed lower concentrations of hydroperoxides due to suppression of HO_2 by NO_x . Despite being a high alpine site, it is believed that for only 4% was truly free tropospheric air sampled during the FREETEX 2003 campaign. Thus deposition to both the surface and to clouds played a significant role in determining the concentrations of hydroperoxides at this site. The concentrations of hydroperoxide measured are consistent with previous box-modelling work for the site only if a significant deposition source is included in the box model. Thus comparisons between these observations and the results of chemical transport models should be carried out carefully to reflect the influence of the boundary layer at this site.

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Hydroperoxides at Jungfraujoch Observatory

S. J. Walker et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

and hospitality. Parts of the measurements were made by the Swiss National Air Pollution Monitoring Network (NABEL) on behalf of the Swiss Federal Office for the Environment (FOEN). The financial support of the NABEL network by FOEN is acknowledged. S. J. Walker would like to thank R. Purvis (now at FAAM, UK), J. Lee (now at University of York, UK) and L. Whalley (University of Leeds, UK) for their generosity and support throughout the campaign. The authors would also like to acknowledge R. Morgan (for his assistance in preparing for the campaign) and S. Arnold (for assistance in the preparation of back-trajectory plots). S. J. Walker acknowledges a NERC studentship (NER/S/S/2002/11165) and A. V. Jackson acknowledges the NERC/AFI grant (RG.ENVI.444968).

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Hydroperoxides at
Jungfraujoch
Observatory

S. J. Walker et al.

Title Page	
Abstract	Introduction
Conclusions	References
Tables	Figures
◀	▶
◀	▶
Back	Close
Full Screen / Esc	
Printer-friendly Version	
Interactive Discussion	

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Hydroperoxides at Jungfraujoch Observatory

S. J. Walker et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Hydroperoxides at Jungfraujoch Observatory

S. J. Walker et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Hydroperoxides at Jungfraujoch Observatory

S. J. Walker et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Hydroperoxides at Jungfraujoch Observatory

S. J. Walker et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Hydroperoxides at Jungfraujoch Observatory

S. J. Walker et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 1. Selected hydroperoxide measurements at high altitude.

Altitude (km a.m.s.l.)	Location	Time of year	Mean H ₂ O ₂ (pptv, range)	Mean (pptv, range)	CH ₃ OOH	Notes
High Altitude Sites						
3.6	Jungfraujoch, Swiss Alps (47° N, 8° E)	Feb–March 2003	206±261 (<21– 1424)	76±96 (<21–921)		This work, no significant diurnal cycle
0.5–5.0	Ground and Airborne, Swiss Plateau/Alps (incl. JFJ, 47° N, 8° E)	June–July 1990 July–Aug 1991	~1400 for JFJ excl. rain/cloud events (<100– 6000)	Not measured (ROOH <300)		No distinct diurnal cycle, air- borne sampling via manned balloon/glider (Dommen et al., 1995; Sigg et al., 1992; and Lehman et al., 1992)
1.2–1.8	Ground, Bavarian Alps, Germany (47° N, 11° E)	June–Sep 1990	~750 (<50–1750)	~100 (<20–550)		Diurnal variation, HOCH ₂ OOH <550 pptv, also detected C ₂ H ₅ OOH and CH ₃ C(O)OOH, total ROOH was 10–40% H ₂ O ₂ (Fels and Junkermann, 1994)
2.8	Mt. Norikura, cen- tral Japan (37° N, 137° E)	July–Sep 1993, 1994	1100±750 for Au- gust (100–4500)	Not measured (ROOH <1000, Semi-quantitative)		Peak H ₂ O ₂ at night (Watanabe et al., 1995)
Airborne						
0.3–13	North Pacific Ocean (0–65° N, 115° E–125° W)	Autumn 1991	<1000 (for >45° N) (<30–6000)	<500 (for >45° N) (<50–3000)		Other ROOHs not detected (<100 pptv) (Heikes et al., 1996a)
0.3–10	South Atlantic and W. Indian Oceans (20° N–40° S, 60° W–40° E)	Sep–Oct 1992	3200±1800 (for MBL to 4 km) (300–6000)	1000±450 (400–1900)		Vertical H ₂ O ₂ profiles (Heikes et al., 1996b)
0–12	Tropical South Pacific (0–30° S, 170° E–110° W)	Sep–Oct 1996	200±110 (0–1600)	80±80 (0–1200)		Vertical H ₂ O ₂ profiles, for 3.5 km, H ₂ O ₂ and CH ₃ OOH ~1100 and ~500 pptv (Cohan et al., 1999)
10	Tropical South Pa- cific (13° S, 152° E)	April 1999	77±21 (50–120)	64±24 (50–500)		(Ravetta et al., 2001)
0.5–3.0	Nashville, Tennessee (36° N, 87° W)	July 1995	2400 (median) (<100–5000)	1700 (median) (500–3750)		Assumed only H ₂ O ₂ , CH ₃ OOH and HOCH ₂ OOH (also detected) were collected (Weinstein-Lloyd et al., 1998)
0.7–3.7	Central Arkansas (35° N, 92° W)	Jan–Oct 1988	~200 winter mean (<10–8000)	Not measured		(Ray et al., 1992)
0–3.5	Eastern U.S. (25– 44° N, 76–89° W)	Oct–Nov 1984	400–1900 (<200–4100)	Not quantitative (ROOH < 500)		Vertical H ₂ O ₂ profiles (Heikes et al., 1987).

Hydroperoxides at Jungfraujoch Observatory

S. J. Walker et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Table 2. Composition of air-masses with varying NO_x to NO_y ratios leading to hydroperoxide production and suppression.

	A) Semi-polluted, SW air-mass	B) Freshly polluted, SW air-mass	C) Photo- chemically aged, SW air-mass	D) NW descending air
Air-mass altitude origin (Table 2 panel, trajectory colour)	Remained at ~650 hPa, some vertical mixing with aged air from >5 km (left panel, black/dark blue)	Ascended from ~800 hPa in last 5 d (left panel, light blue/green)	Descended from ~500 hPa in last 5 d (right panel, dark/light blue)	Descended from ~500 hPa in last 5 d (top panel, green/orange)
Start time	00:00 6 March	08:00 6 March	07:00 11 March	14:00 9 March
Relative humidity (%)	~50	>80	<20	30–80
NO_x/NO_y	0.6	0.8	0.3	0.4
NO (pptv)	<93	≤510	<40	<30
CO (ppbv)	95–134	≤193	112–147	120–150
O ₃ (ppbv)	45–55	25–40	50–65	54–58
H ₂ O ₂ (pptv)	≤1010	<75	≤1424	≤682
CH ₃ OOH (pptv)	≤440	<85	≤922	≤392

Hydroperoxides at Jungfraujoch Observatory

S. J. Walker et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Hydroperoxides at Jungfraujoch Observatory

S. J. Walker et al.

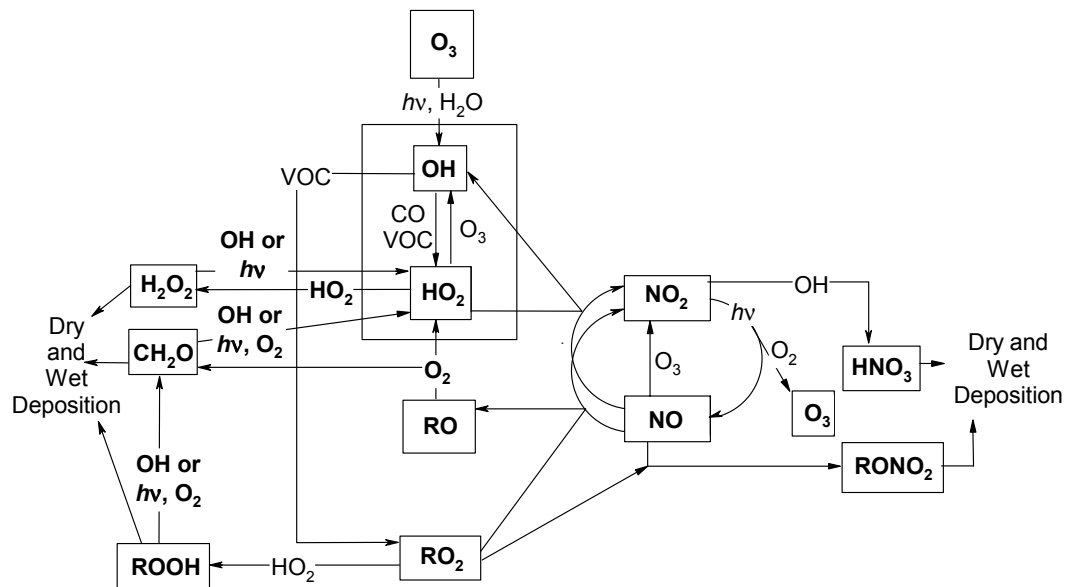


Fig. 1. Tropospheric gas-phase reactions linked to hydroperoxides.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Hydroperoxides at Jungfrauoch Observatory

S. J. Walker et al.

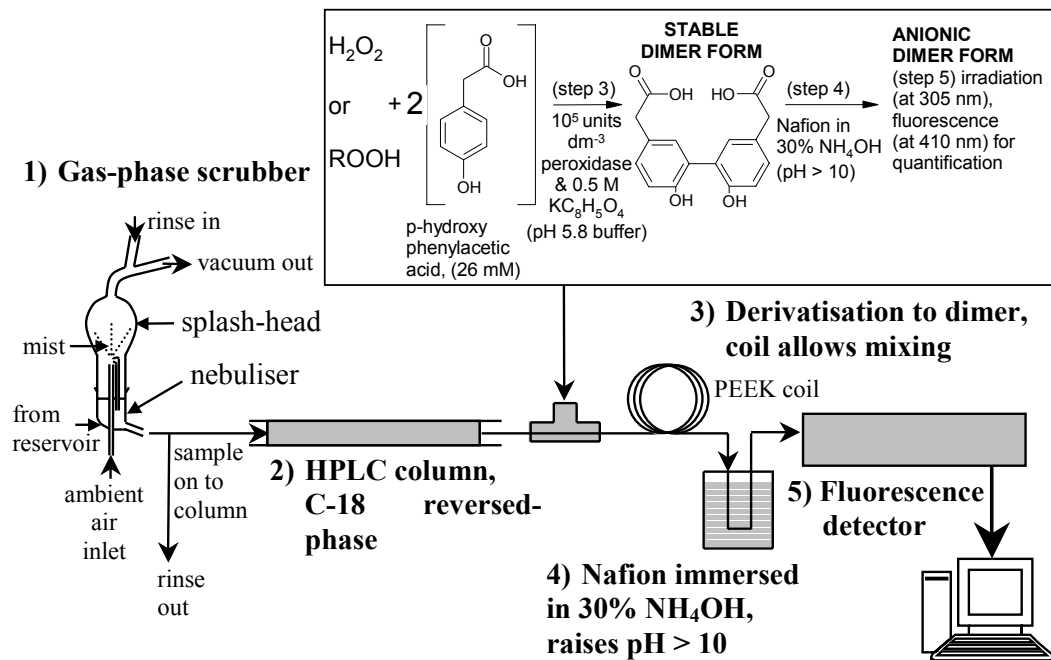


Fig. 2. Schematic diagram of gas-phase sampling and analysis of hydroperoxides using a nebulising reflux concentrator, HPLC and post-column derivatisation.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Hydroperoxides at
Jungfraujoch
Observatory**

S. J. Walker et al.

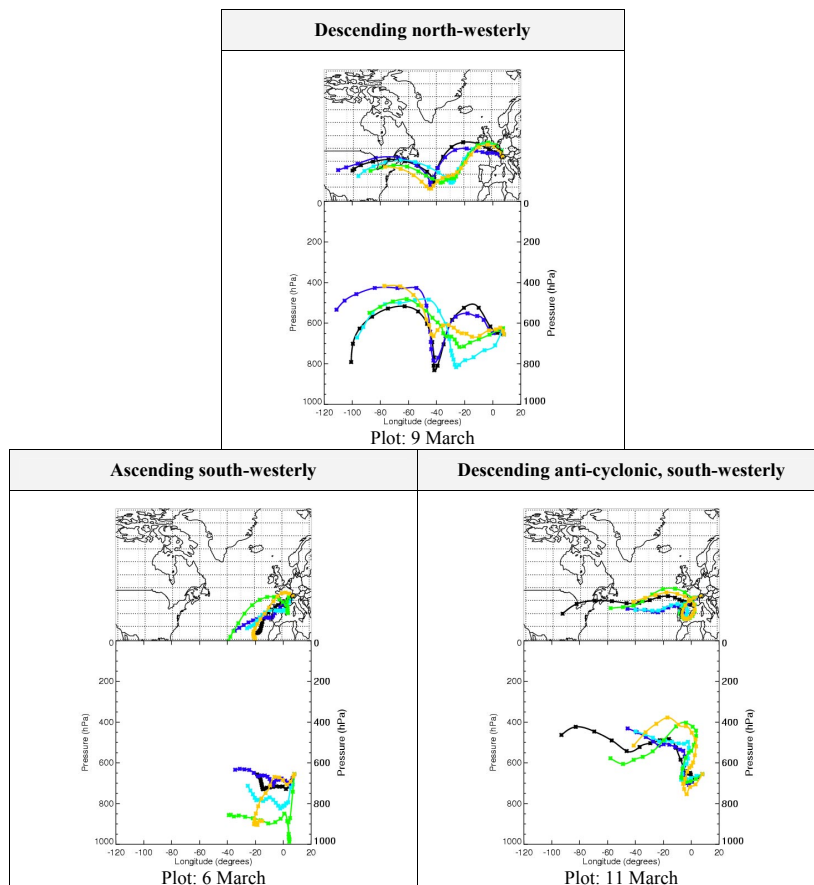


Fig. 3. Typical 5-day back-trajectories of air-masses sampled at JFJ (provided by the BADC Trajectory Server). Arrival dates of trajectories are shown. Trajectory release times are 00:00 (black), 06:00 (dark blue), 12:00 (light blue), 18:00 (green) and 24:00 (orange) in GMT. Crosses are every 6 h along trajectory.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Hydroperoxides at Jungfraujoch Observatory

S. J. Walker et al.

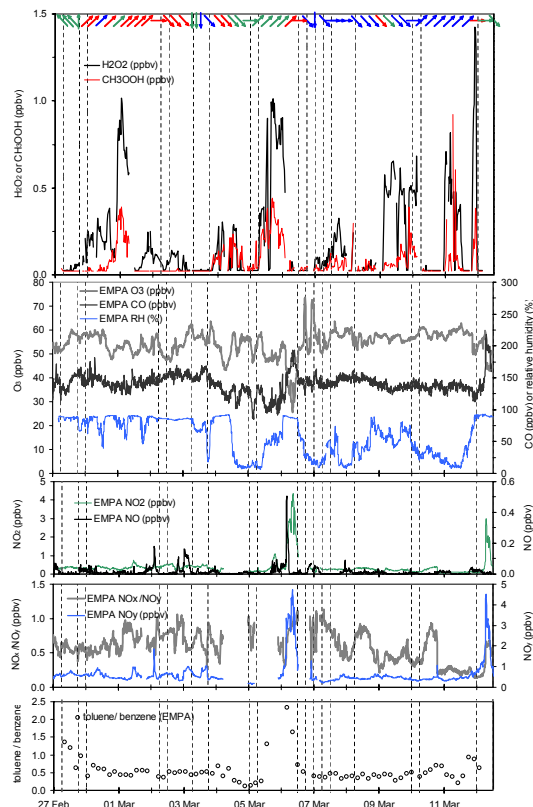


Fig. 4. Time series of H_2O_2 , CH_3OOH , O_3 , CO , relative humidity (RH), NO_2 , NO , NO_x to NO_y ratio, NO_y and the toluene to benzene ratio. Arrows in top panel and dashed vertical lines indicate changes in the prevailing wind direction deduced from the last day of 5-day back-trajectories (see Sect. 3.2 for further details). Descending air from >3.6 km (blue arrows), ascending air from <2 km (red arrows) and level (green arrows) indicates air that had remained at constant altitude for the last 5 days. Local NO and toluene contamination has been removed. Tick marks on time axis refer to noon (GMT).

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[I◀](#)
[▶I](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

Hydroperoxides at Jungfraujoch Observatory

S. J. Walker et al.

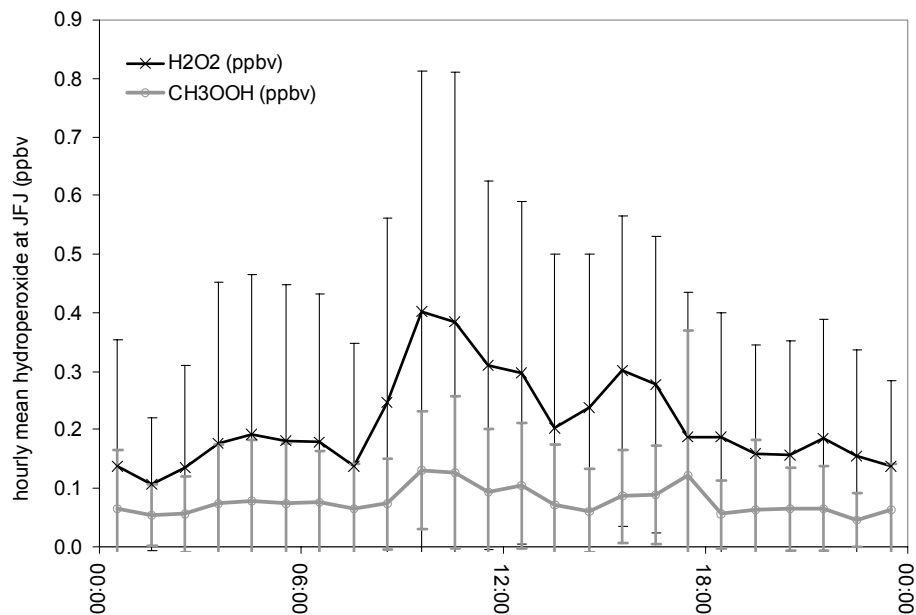


Fig. 5. Mean diurnal cycles for H_2O_2 (black crosses/line) and CH_3OOH (grey points/line) where error bars show 1 standard deviation.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)